ESB Incorporated
The Carl F. Norberg Research Center
Yardley, Pennsylvania
The Exide Missile and Electronics Division
Raleigh, North Carolina

HEAT STERILIZABLE, IMPACT RESISTANT CELL DEVELOPMENT

JET PROPULSION LABORATORY
CONTRACT No. 951296

REPORT FOR FIRST QUARTER 1968
JANUARY 1 TO MARCH 31, 1968

"This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100."

Edited by G. W. Bodamer
G. W. BODAMER
Program Director

Approved by R. A. Schaefer
R. A. SCHAEFER
Director of Research

JULY 15, 1968

NOTICE

This report was prepared as an account of Government - sponsored work. Neither the United States, nor the National Aeronautics and Space Administration (NASA), nor any person acting on behalf of NASA:

(a) Makes warranty or representation, expressed or implied with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately - owned rights; or

(b) Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used above, "person acting on behalf of NASA" includes any employee or contractor of NASA, or employee of such contractor, to the extent that such employees or contractor of NASA, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment with such contractor.

Requests for copies of this report should be referred to:

National Aeronautics and Space Administration
Office of Scientific and Technical Information
Washington 25, D. C.

Attention: AFSS-A

HEAT STERILIZABLE, IMPACT RESISTANT CELL DEVELOPMENT

JET PROPULSION LABORATORY
CONTRACT NO. 951296

REPORT FOR FIRST QUARTER 1968
JANUARY 1 TO MARCH 31, 1968

ABSTRACT

Electrochemical studies during the first quarter of 1968 have been directed toward establishing the sources of capacity loss following heat sterilization of sealed cells. The effect of pack tightness was not clear within the limits examined. On the other hand, it was quite plain that longer sterilization periods cause greater losses than shorter periods. Initial work on the possible contribution of organic components has been ambiguous, and the experimental apparatus has been redesigned. The investigation of SWRI-GX separator performance in sterilized silver-cadmium cells on cycle, charged stand, and float has been completed, and a final summary is included in this report. A float regime appears best for long life.

Engineering studies of the use of Inconel, zirconium, and silver-boron filament composite have been begun with the aim of providing increased shock resistance for those cells carrying such requirements. Investigation of heat sterilizable, high cycle life batteries is in the early planning stage. The development of the soft landing 2000 watt-hour battery is on schedule.

TABLE OF CONTENTS

TABLES

TABLES (continued)

FIGURES

ELECTROCHEMISTRY

I. INTRODUCTION

Many of the problems associated with electrodes, electrolytes, separators, cases, sealants, and so on, as separate components have been solved. However, unforeseen phenomena have appeared and have been reported when components were sterilized in the form of full cell assemblies, especially when these cells were sealed before sterilization. Recent studies have been directed toward identifying the cause of capacity losses under such conditions and in providing supporting plate structures which will not lead to gassing.

The study of the performance of separator material following sterilization in silver-cadmium cells has been completed, and a final summary of this work concludes this section.

II. FACTORS WHICH MAY AFFECT CAPACITY

A. Electrolyte Concentration and Cell Pack Tightness

Table I gives capacity data for two electrolyte concentrations and two degrees of pack tightness.

In early cycles there does not appear to be a clear-cut advantage for either 41% KOH or 35% KOH, both saturated with ZnO. In later cycles the capacity seems to be consistently higher for 41% KOH.

Similarly, pack tightness does not seem to be a significantly influential factor in early cycles, though in later cycles there is perhaps some advantage in tighter cell packs.

Comments made in the last quarterly report on earlier portions of this same data may be valid, but appear inconsequential compared to consistent capacity losses described in the next section.

B. Duration of Heat Sterilization

Table II shows the effect of time at the sterilization temperature of 135°C on sealed-then-sterilized cells.

For comparison with previous cell data, on the first discharge of cells sterilized 72 hours, the low capacity was 4.7 amp-hrs (69-3) and the high 5.6 amp-hrs (62-2); sterilized 120 hours, low capacity 4.4 amp-hrs (74-2, -3, and -4) and the high 4.7 amp-hrs (69-6).

TABLE I

Effect of KOH Concentration and Pack Tightness on Sterilized-then-Sealed Ag-Zn Cells (1)

Cell Number	201	202	204	208	209	210	214	215	216	218	219	220
Electrolyte Concentration (per cent KOH before saturation with ZnO)	35	35	35	41	41	41	41	41	41	35	35	35
Thickness per separator layer ($X10^{-3}$ in)	2.6	2.6	2.6	2.6	2.6	2.6	2.1	2.1	2.1	2.1	2.1	2.1
Capacity in Amp. hr.												
First Discharge	5.90	5.14	6.25	6.12	5.75	6.00	5.88	5.63	5.51	5.35	5.77	5.90
Second	5.66	5.76	5.86	5.47	5.74	5.55	6.05	5.90	5.79	5.43	6.06	5.89
Third	6.06	6.21	6.15	5.61	5.74	5.40	5.60	5.60	5.65	5.68	5.95	6.03
Fourth	6.13	6.39	6.31	5.97	6.22	5.76	5.97	5.83	5.63	5.95	6.09	5.85
Fifth (2)	6.24	6.24	6.24	5.68	5.68	5.68	5.68	5.79	5.67	5.90	6.17	6.07
Sixth (3)	6.01	6.01	6.01	5.70	5.70	5.70	5.55	5.55	5.55	5.71	5.71	5.71
Seventh	6.29	6.29	6.29	5.88	5.88	5.88	5.51	5.51	5.51	5.97	5.97	5.97
Eighth	6.24	6.24	6.24	5.79	5.79	5.79	5.58	5.58	5.58	5.67	5.67	5.67
Ninth	5.97	5.97	5.97	5.76	5.76	5.76	5.67	5.67	5.67	6.06	6.06	6.60
Tenth	5.90	5.90	5.90	5.91	5.91	5.91	5.51	5.63	5.32	6.04	6.19	5.92
Eleventh	5.90	5.90	5.90	5.90	5.90	5.90	6.50	6.48	6.50	5.99	6.45	5.58
Twelfth	6.05	6.08	5.87	6.03	5.84	5.79						
Thirteenth	6.21	5.85	5.65	6.56	6.35	6.33						

(1) All negatives contained 7% Compound 323-43 and 2% Teflon

(2) Cells with separator thickness 2.6×10^{-3} in. were cycled as 3-cell batteries from fifth through eleventh cycle.

(3) Cells with separator thickness 2.1×10^{-3} in. were cycled as 3-cell batteries from sixth through ninth cycle.

TABLE II
Effect of Sterilization Time on Sealed-then-Sterilized Cells

72 Hours at 135°C	Amp-Hr/g Ag on Discharge No.			
Cell No.	1	2	3	4
61-3	0.31	0.31	0.29	0.29
62-1	0.30	0.30	0.29	0.31
62-2	0.32	0.32	0.32	0.31
69-1	0.31	0.31	0.31	0.31
69-3	0.27	0.27	0.28	0.29
69-4	0.29	0.28	0.28	0.30
120 Hours at 135°C				
69-6	0.26	0.25	0.27	0.26
69-7	0.25	0.25	0.27	0.26
69-8	0.23	0.23	0.20	0.20
74-1	ND	0.22	0.18	0.19
74-2	0.25	0.27	0.26	0.26
74-3	0.25	0.27	0.25	0.25
74-4	0.26	0.27	0.26	0.26

Compared to cells sterilized at 135°C for 120 hours before sealing, those sealed-then-sterilized for 72 hours have lost as much as 10% of their capacity, and those sealed-then-sterilized for 120 hours have lost from 4 to 24% of their capacity. Thus sterilization alone has not caused the great capacity loss, but rather sterilization in the sealed condition. It is felt that the latter operation retains harmful volatile materials coming from some of the organic components.

C. Organic Components

The data in the previous section was obtained from cells assembled in PPO 534-801 cases, sealed with epoxy DEN438 EK85-DMP 30, and using only SWRI-GX as the separator-absorber-retainer system. Prior work with six sterilized-then-sealed cells had shown that omitting EM-476 gave first discharge capacities of 6.4 to 6.7 amp-hours per cell vs. six comparable cells containing EM-476 which gave 5.6 to 6.0 amp-hours.

Thus it has become increasingly necessary to study this system in an assembly that will permit examination of as few organic components at one time as possible. Several models of the nickel bomb-Teflon insert assembly described and depicted in the last quarterly report were constructed during the past quarter. Four cells were made in this type of equipment having SWRI-GX separator and EM-476 absorber but with no PPO or epoxy present. Two were unsterilized (though sealed) and two were sealed-then-sterilized at 135°C for 120 hours. Capacities were as shown in Table III.

TABLE III
Effect of SWRI-GX and EM-476 in Sealed Cells

	Unsterilized		Sterilized	
	434-80-1	434-80-2	434-80-5	434-80-6
Amp-Hrs/g Ag				
First Disch.	0.34	0.32	0.33	0.33
Second Disch.	0.33	0.30	0.33	0.32

The anticipated bad effect of EM-476 when sterilized was not observed. In fact all capacities were reasonably good. However, it was noted that the free space above the Teflon insert was much greater than the normal head space that would be present in an actual sealed cell. This might mask effects of volatile substances such as organic amines or ammonia should they be the cause of capacity losses. Therefore, new Teflon inserts have been designed to occupy as much space within the nickel bombs as possible. These assemblies will be used to continue the experiments outlined last quarter.

III. FACTORS AFFECTING GASSING. GRID SUPPORTS

A. Evaluation of Float Current and Overvoltage of Silver Electrodes

Since the cells to be developed under this contract will probably be floated, it is advantageous to have information on the float currents of electrodes containing various reinforcing members. Positive electrode assemblies as indicated in Table IV were sterilized and then had their float currents measured at a constant 1.5 volt potential vs. nickel antipodes. The difference in amount of current flowing was not significant within the accuracy of the experiment. Therefore none of these assemblies would be expected to produce gas during a floating regime.

After the float test, the overvoltages were measured on these electrodes, and the data at 20 and 100 milliamps are shown in Table V. These data also lead to the conclusion that none of these reinforced electrodes should produce gas during float, since their overvoltages are higher than a standard electrode without reinforcement.

B. Oxidized Zirconium As Negative Grid Support

In order to check the suspicion mentioned in the last quarterly report (p. 26) that this was an unsatisfactory construction, a test was performed to compare the overvoltage of an electrode having standard silver grid with one having an oxidized zirconium grid. Both electrodes were prepared by pressing active negative mix onto the grids in the usual manner. The electrodes were formed using the slow pre-formation charge to a 1.45 volt cutoff followed by the 5 mA/in^2 to 2.02 volts charge, discharged 20% and then charged to 2.02 volts at 5.6 mA/in^2. The results were as follows:

	Voltage	
Current (mA)	Std. Neg. Electrode	Oxidized Zr
20	1.54	1.42
60	1.58	1.46
100	1.70	1.49

The overpotential of the oxidized zirconium is lower at every level of current that that of the standard electrode and consequently, other factors being equal, electrodes with zirconium in the negative should yield more gas when used in cells. Recent cell data appear to support the above conclusion and therefore oxidized zirconium is not recommended for the negative electrode although silver-plated zirconium in the positive may be acceptable. See Table VI.

TABLE IV
Float Test on Reinforced Silver Electrodes

Reinforcement	Current (microamps) at Various Times (hrs)				
	0.8	113	140	334	450
None	400	225		200	
Silver Sheet	250	160		200	
Zirconium	400	250		200	
Silver-Plated Zirconium			370		250
Inconel			325		325
Silver-Plated Inconel	350	425		300	

TABLE V
Overvoltage of Reinforced Silver Electrodes

Reinforcement	Voltages			
	20 ma		100 ma	
	1	2	1	2
None	0.55	0.54	0.62	0.61
Silver Sheet	0.61	0.61	0.66	0.66
Zirconium	0.60	0.60	0.71	0.71
Silver-Plated Zirconium	0.59	0.60	0.68	0.68
Inconel	0.56	0.56	0.62	0.62
Silver-Plated Inconel	0.57	0.57	0.63	0.63

TABLE VI

Average Capacity* of Sealed Then Sterilized Cells with Zirconium Supports in the Plates

	1st Cycle		2nd Cycle		3rd Cycle		4th Cycle	
	Zr in both	Zr in Pos.	Zr in both	Zr in Pos.	Zr in both	Zr in Pos.	Zr in both	Zr in Pos.
Pre-formation Capacity (AH)	0.30	0.28	0.0	0.0	0.0	0.0	0.0	0.0
1-Stage Chg. Cap. (AH)	2.51	4.03	2.95	3.24	2.49	3.59	2.86	3.64
2-State Chg. Cap. (AH)	1.79	1.58	1.25	1.98	0.87	1.39	0.93	1.11
** Net Chg. Cap. (AH)	3.81	4.89	3.42	4.53	2.78	4.26	3.20	4.10
1-Stage Dischg. Cap. (AH)	2.26	2.70	2.34	3.32	2.39	3.44	2.56	3.44
Midvoltage	1.40	1.40	1.40	1.41	1.40	1.43	1.42	1.45
2-Stage Dischg. Cap. (AH)	0.38	0.85	0.33	0.60	0.26	0.50	0.30	0.29
Total Dischg. Cap. (AH)	2.64	3.55	2.67	3.90	2.65	3.94	2.86	3.73
Output/Input	.70	.72	.75	.86	.96	.93	.89	.91
AH/g Ag	.21	.26	.21	.29	.21	.29	.23	.29

* Average of four cells each.

** Net charge is the sum of the pre-formation charge, the first stage charge minus 20%, and the second stage charge capacities.

C. Pinhole Test for Plated Cell Parts Using Overvoltage

As discussed above, most of the metals which offer the best strength have a pernicious effect on either the capacity or the pressure produced in the cell, unless the metals are silver plated. But even when these metals are silver plated the deleterious effects are not always overcome because of pin holes formed during the plating process. It is highly desirable to have a rapid test to discern the presence of pinholes. A simple but useful method which takes advantage of the overpotentials of the electrodes was developed. The procedure is as follows.

After an electrode has been silver plated and the leads are attached, the overvoltage is measured at two currents, namely 20 and 100 mA, and the presence of a pinhole is assessed by comparing the overvoltage to a silver sheet of the same size which was silver plated. An example of the test is illustrated in Table VII where the data show that the lower overvoltage surface is controlling when two pieces of metal of different overvoltages are connected in parallel. For the case of the metals which were silver plated, as long as the metal has a lower overvoltage surface than silver, the overvoltage will correspond to the metal if a pinhole is present whereas it will correspond to silver in the absence of a pinhole. It is assumed that if a pinhole is so small that it does not affect the overvoltage then this electrode should behave as if the pinhole were absent and should have no detrimental effect on the cell due to electrical considerations.

TABLE VII
Pinhole Test Using Overvoltage

Material	Voltage of Electrode vs. Hg-HgO as Function of Current	
	20 mA	100 mA
Ni	1.10	1.14
Cu	1.34	1.38
Ni and Cu	1.10	1.16

IV. STAND LIFE OF Ag-Zn CELLS STERILIZED THEN SEALED

Another cell parameter of importance is the stand life. Although there are some unanswered questions regarding the performance of cells sealed-then-sterilized as compared with cells sterilized-then-sealed, the data shown in Table VIII for cells sterilized-then-sealed may indicate the kind of performance to be expected. The data are for pairs of cells after 7, 8, and 9 months' open circuit stand at room temperature. Capacity loss per month as a percent of total capacity varied from 0 to 1.3.

TABLE VIII

Stand Retention Data on Sterilized-then-Sealed Silver-Zinc Cells

Cell Number	99	109	100	110	101	111
Capacity before stand (amp. hrs.)	6.20	5.20	5.8	4.5	6.0	5.3
Days on stand	216	216	245	245	277	277
OCV after stand	1.858	1.854	1.858	1.858	1.857	1.858
Capacity after stand (amp. hr.)	5.67	4.72	5.76	4.98	5.7	4.7
Loss in capacity during stand (amp. hr.	0.53	0.48	0.04	-	0.3	0.6
Percent loss per month	1.2	1.3	0.08	-	0.5	1.2

V. PERFORMANCE OF SEPARATOR FOLLOWING STERILIZATION IN SILVER-CADMIUM CELLS

A. Introduction

The experimental work reported under this task was undertaken in response to a request from JPL to examine the effects of sterilization on separator performance in the possible battery flight conditions during the mission. These were seen to be (1) cycle duty, (2) charged stand, or (3) constant potential float. The test program which evolved is shown in Figure 1. The testing was to include a number of different separator materials including (1) RAI Permion 116, (2) fibrous sausage casing, and (3) a modified poly benzimidazole film (Narmco Division of Whittaker Corporation).

An initial examination of the effect of sterilization at 135°C on fibrous sausage casing indicated degradation and solubilization of this material in the electrolyte. On this basis, fibrous sausage casing was excluded from consideration. The modified poly benzimidazole film was unavailable since its development was not far enough along to provide the necessary quantity of film.

The program thus became limited to the Permion 116 material. This was later changed to a chemically similar separator produced at the Southwest Research Institute and designated SWRI-GX. The substitution was made on the basis of comparative bench testing of both materials. The shipment of separator material originally designated for this experiment (RAI-116 Rolls 14, 15, 16) varied in electrical resistance beyond the manufacturer's specifications. Replacement RAI-116 submitted by the supplier was found to be much more uniform. At the same time, SWRI-GX film was submitted by JPL and found to be more uniform in resistance, both in testing here and at JPL. Since adequate quantities of SWRI material were immediately available to JPL, the substitution of SWRI-GX for Permion 116 was made in the program.

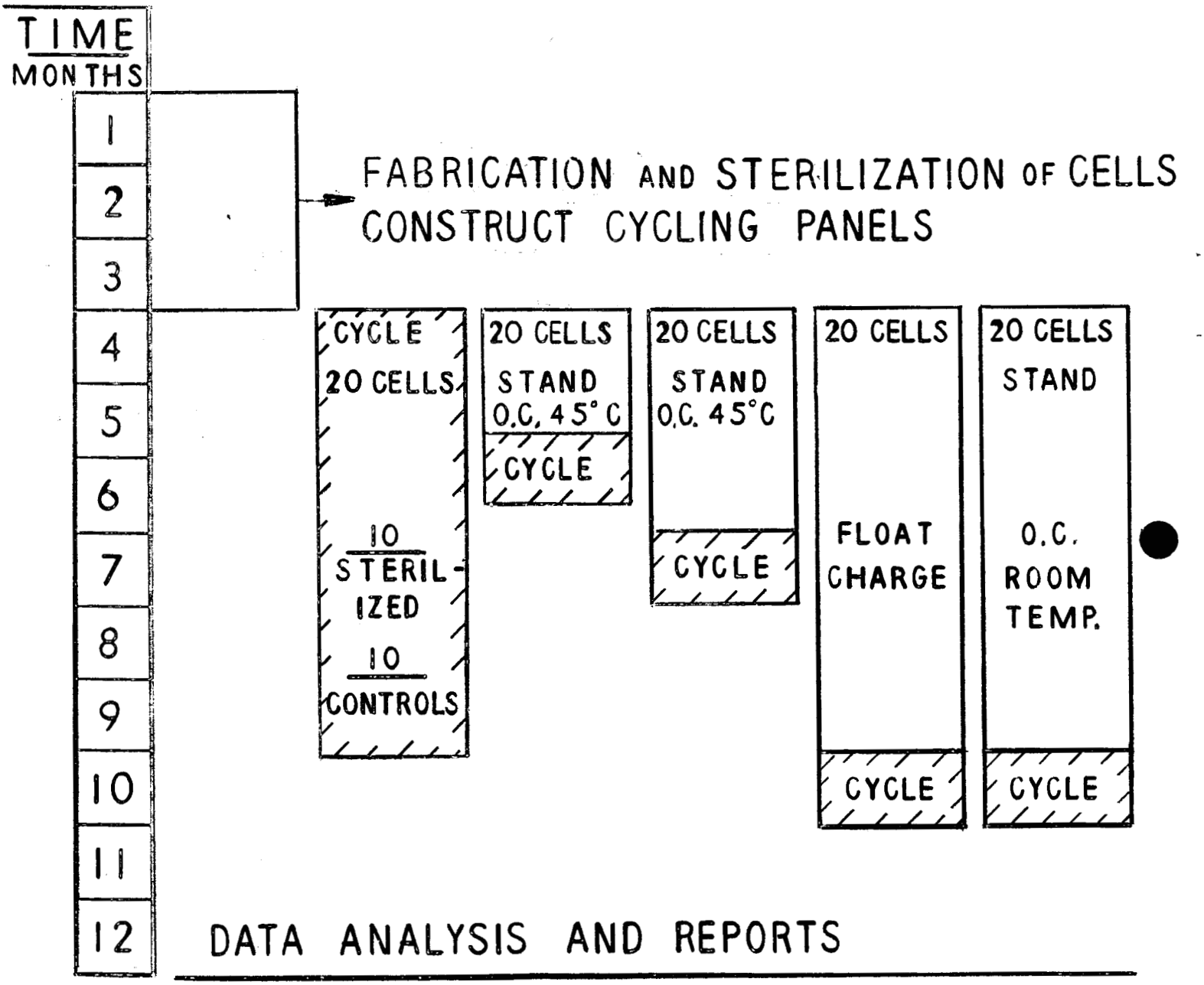
B. Cell Construction

The experimental plan called for simultaneous testing of cell groups which had been subjected to sterilization conditions (135°C, 120 hours in 40% KOH) and those which had not been so treated. These latter served as the controls.

Since case materials and seals capable of withstanding sterilization conditions had not been completely developed at that time, sterilization was performed in nickel containers holding eight fully assembled three-plate cell stacks. Three nickel containers were inserted into a three-liter stainless steel bomb. The 40% KOH electrolyte level was placed

FIGURE 1

SEPARATOR TEST PROGRAM SCHEDULE



above the plate tops in each container and the lot sterilized in an air circulating oven (120 hours at 135°C). Bomb leakage with consequent concentration of the electrolyte caused rejection of the first lot of sterilized cell stacks, but subsequent runs were processed uneventfully. It is of interest to note that in the rejected lot of cells severe inhibition of charge acceptance was apparently the result of the sterilization in the higher KOH concentration (measured 48% as the average concentration of three containers).

Fifty sterilized stacks were shimmed and placed into standard S 7.5 polystyrene cell jars. These sterilized cells, together with an equal number of control cells, were formed open and flooded to the plate tops using constant current charging.

The formation charge was sufficient to overcharge the silver electrode while providing only 78% of the theoretical cadmium electrode capacity. While still unsealed, the cells were discharged, charged using a modified taper charge 1.60 v/cell with current limited to 0.4 A, and again discharged. The latter cycle was repeated. Electrolyte was then removed to provide the final level at one-third plate height, the cells were sealed in five-cell batteries by overpotting with epoxy, and four batteries (Two controls, two sterilized) were placed in each test.

The pertinent data concerning cell construction is given in Table IX. In the first three cycles the average capacity of the control cells were 1.51 ± 0.20 ampere-hours with a range of 0.63 ampere-hours while the sterilized cells averaged 1.82 ± 0.25 with a range of 0.57 ampere-hours.

C. Test Regimes

1. Continuous Cycle

Cycling panels were constructed to conduct this experiment. Each panel tested a single five-cell battery through constant current discharge and subsequent modified c.p. recharge. Discharge was conducted with the five cells in series, with discharge cut-off when the weakest cell reached 0.60 volt. In the charge mode, the five cells were in series, with charge cut-off when an individual cell reached a charge voltage of 1.70 volt. Thus the weakest cells limited battery performance.

The performance of the cycled cells is given in Table IXa. The sterilized batteries gave better capacity and more uniform performance on a cell-to-cell basis than did the controls for the first fifty cycles. At cycle 62, there were indications that the open circuit voltage of three of the sterilized cells was not being maintained during a two-day stand resulting from failure to complete the charging cycle. A malfunction of the cycling panel at cycles 81, 82, 83 caused reversal of four of five cells in Battery 4.

TABLE IX
Constructional Details
Three Plate Silver Cadmium Cells

1. Positive Plate

Grid	2/0 Ag
Active Material Wt.	6.25 g
Dimensions, inches	1.75 x 1.875 x .028
No. per cell	1
Retainer	1 EM476
Membrane	6 SWRI-GX

2. Negative Plate

Grid	2/0 Ag
Active Material Wt.	6.3 g CdO (plus 0.70 g Ni powder)
Dimensions, inches	1.75 x 1.875 x 0.050
No. per cell	2
Absorber	1 EM476

3. Membrane Separator Expansion Factor in 40% KOH
   - Sterilized 1.5 - 1.8
   - Non-sterilized 1.1 - 1.5

   For calculating pack tightness an S.E.F. of 2.5 was used for all cells.

4. Electrolyte - 40% KOH

5. Recombining Electrodes - Silver Electrodes, 1.75 x 1.875 x .010 inches, placed outside of and connected to negative electrodes.

6. Shim Material - Polysulfone sheet .011 and .091 inch

7. Outside Spacer -

Thickness	20 mesh polypropylene screen .046 inch
Placement	Between recombining electrode and shim stock.

TABLE IXa
AgO-Cd Sealed Cells - Cycling Test

Conditions

1. Charge c.p. 8.00 volts/battery
   duration 18 hours
   current limited to 0.4 amp
   Charge cut off if individual cell voltage exceeded 1.73 v
2. Discharge - Constant current -0.50 amp (1)
   duration - 3 hours or until an individual cell voltage fell below 0.60 v
3. Open circuit - minimum 2 hours between charge-discharge; 1 hour between discharge-charge

Battery	Capacity in Amp-hours at Cycle Number Shown															
	1	10	25	45	65	80	90	100	110	120	130	140	150	160	170	180
1. in	-	1.56	1.69	1.27	1.41											
out	1.13	1.27	1.20	1.20	1.17	1.12										
							1.12	1.06	1.20	1.0	1.01	0.66	0.96	0.96	1.00	1.00
2. in		1.62	1.86	1.52	1.80											
out	1.13	1.20	1.20	1.18	1.20	1.20										
							1.20	1.20	1.20	1.17	1.17	1.07	1.17	1.17	1.20	1.17
3. in		1.58	1.68	1.87	1.95											
out	1.50	1.50	1.50	1.40	1.20	0.40										
							0.14	-								
4. in		1.59	1.96	1.43	1.97											
out	1.50	1.47	1.27	1.20	1.00	0.40										
							-	-								

(1) Current reduced to 0.40A at cycle 46

Since these did not recover on subsequent cycles this battery was removed from cycle and post-mortemed. The separators removed from these cells were intact with no tears or pinholes but were heavily stained with silver (2.3 - 8.6 Mg Ag/layer). Both positive and negative plates were in the discharged state.

At cycle 80 Battery 3, also sterilized, gave poor capacity and abnormally low charge voltages. A manual cycle confirmed that the cells could not satisfactorily charge, and this battery was also removed from the cycling experiment. The examination of the separators and electrodes from two of these cells confirmed the observations on Battery 4.

The control cells completed 180 cycles after which a manual discharge at 0.40 amperes yielded individual cell capacities of 0.90 to 1.55 ampere hours for the ten cells of Batteries 1 and 2.

Sterilization adversely affected the cycle life of these cells.

2. Charged Stand

As originally conceived, the effect of charged stand on cell performance was to be measured both at ambient temperature and at 45°C. Stand times of 6 and 12 weeks were programmed at the 45° temperature with 180 days the duration at room temperature. Correlation between the data at the two temperatures was of interest in predicting the effect of charged stands at ambient temperature but of longer durations than encompassed in this test.

Open circuit voltage was monitored daily on the stand cells. The OCV of the sterilized cells both at ambient and at 45°C rapidly decayed from the original 1.40 - 1.41 volts per cell. At the six week period 13 of 20 sterilized cells had OCV's below that usually assigned to the Ag_2O-Cd couple. Of the 10 sterilized cells scheduled for discharge at the six week point, only 4 yielded capacity on discharge while all 10 control cells retained capacity ranging from 33% to 75.3% of original capacity.

Of the 12-week stand cells, only 2 sterilized and 3 controls, gave useful capacities (0.75 and 1.0 amp-hrs sterilized; 1.30, 0.42 and 0.20 controls), but, significantly, on recharge only the control cells could be recharged to a stable open circuit voltage. Inspection of the separators in the sterilized cells revealed blackening of all separator layers (5.7 to 2.1 mg Ag/layer) apparently causing shorting.

Since the sterilized cells were inoperative the decision was made to forego cycling of the remaining control cells.

The capacity retention data on these cells is too sparse to lead to any useful extrapolations of charged stand characteristics, except to note

that sterilization of the cell is disadvantageous to charged stand life when compared to non-sterilized components.

The same conclusion can be drawn from the stand test data obtained at ambient temperature. Open circuit voltage declined more rapidly for sterilized cells. All 10 control cells retained 40% or better of original capacity, while only 2 out of 10 sterilized cells gave any capacity after 180 days. On recharge only those two cells could be recharged normally.

3. Float Test

The remaining test mode involved floating the test batteries at 1.60 volts per cell. This test was also performed on four five-cell batteries - two control and two sterilized. A constant potential of 8.00 volts was applied to each battery, and the voltage of each cell, and the pressure of the middle cell of each battery was monitored. Higher pressures were observed for the control cells (35 and 90 psig compared to 30 and 10 psig). After 180 days, the batteries were discharged, given one manual cycle, and then cycled using the automatic cycling equipment for thirty cycles. One cell in each sterilized battery was found to limit battery discharge, and each was cut out of the circuit at cycle 23 while cycling continued on the remaining cells. The data on the discharge from float and subsequent cycling is given in Table IXb.

From the results of this testing the following conclusions are offered.

(1) The sterilized cells gave more uniform performance and better capacity for the first 50 cycles.

(2) Cycle life was reduced by sterilization by as much as 50%.

(3) Charged stand life was substantially poorer for sterilized cells with shorting caused by silver penetration of the separators the presumed cause.

(4) Of the modes examined, float service offers the best possibility of capacity maintenance for extended storage periods.

TABLE IXb
Three-Plate AgO-Cd Sealed Cells
180-Day Float Test at 1.60 v per cell
Capacity in Ampere-Hours

Unsterilized	Discharge	Recharge	Discharge on Automatic Cycle 1	10	20	30
98	1.33	1.12				
100	1.24	1.13				
104	1.38	1.13				
105	1.55	1.13				
122	1.71	1.13	1.2	1.2	1.2	1.2
99	1.03	1.59				
101	1.29	1.71				
116	1.45	1.90				
129	1.53	1.81				
136	1.44	1.73	1.2	1.2	1.2	1.2
Sterilized						
95	1.63	1.77				
177	1.34	1.53				
196	1.43	1.67				
175	1.47	1.66				
173	1.16	1.71	1.2	1.2	0.91*	1.2
143	1.32	1.55				
149	1.14	1.85				
151	1.19	1.91				
171	1.44	1.76				
122	1.47	1.75	1.2	1.2	0.53**	1.2

* Cell 173 limiting discharge - removed from cycle at cycle 23.

** Cells 149 and 151 limiting discharge - removed from cycle at cycle 23.

FABRICATION AND TESTING OF CELLS

I. FABRICATION AND TESTING OF 25 AH CELLS

A. Objectives and Past Development

Design goals for this task were to develop and test non-magnetic 25-50 AH sealed Ag-ZnO cells capable of wet heat sterilization at 135°C for 120 hours, charge, pre-flight test, 8 month charged life (on float or stand) during a deep space mission, a planet landing impact at 2,800 ± 200 g from 113 ± 2 ft. per second in any axis, and 4 cycles after impact. Table X summarizes previous cell designs and shock test results. While previous shock tests have been directed at a goal of 5,000 g 3 msec. shock capability, observations, failure modes and stress analyses have shown that light weight polysulfone and polyphenylene oxide plate reinforcements would not support plate weights reliably. Recent tests have shown silver metal struts, while electrochemically desirable, would support plates up to 2,400 "g" shocks and 5 AH cell capacity. Above 5 AH capacity or 2,400 "g", metals with higher stiffness factors would be necessary. Inconel and zirconium were selected (1) for advanced cell design testing and silver-boron composites for feasibility tests.

B. High Impact-Heat Sterilizable 25 AH Cells

Inconel 600 plate structures were designed for the Model 365 cell with PPO frames cemented along the bottom and vertical sides of the plates to provide maximum support for shock. A proofing test on silver-plated Inconel 600 was performed by sterilizing two sintered, uncharged positive plate assemblies for 120 hours at 135°C in cell cases containing J40 electrolyte (40% KOH with 91 g ZnO/liter) and sealed with pressure gages. Pressures observed were:

	Pressures (psig)		
Cell No.	Maximum at 135°C	120 Hr. Reading at 135°C	Post-Sterilization at 25°C
5	30.5	24.5	0 or less
6	28.0	21.5	0 or less

No electrolyte leakage and no positive residual pressure from hydrogen generation by interaction of Inconel and the J40 alkaline electrolyte was observed. Hydrogen evolution in positives thus does not appear to be a

(1) Report for Fourth Quarter 1967, JPL Contract 951296, p. 32.

TABLE X

DESIGN OF MODEL 281 HEAT STERILIZABLE
NON-IMPACT CELL vs HIGH IMPACT MODEL 344

DESIGN FEATURE	MODEL 281	MODEL 344
1. Positive Plates -		
Number	6	6
Dimensions, WxHxT, Inches	1.50x1.88x.027	1.50x1.88x.033
Core Material for Shock Support	2/0 Ag grid	.010 perforated Ag Sheet -2/0 Ag grid both sides
2. Negative Plates -		
Number	7	7
Dimensions, WxHxT, Inches	1.50x1.88x.044	1.50x1.88x.045
Core Material	2/0 Ag grid	.010 perforated Ag Sheet -2/0 Ag grid both sides
3. Theoretical Capacity, AH		
Ag	14.5	11.6
ZnO	16.5	11.4
4. Input, Expected		
Positive Limited, AH	13.2	10.2
5. Discharge Output*, Minimum, AH		
Non-Sterile	8.8	6.8
Sterilized 120 hrs. 135°C	6.7	5.2
6. Separator System		
Location "U" fold	On positive	On positive
Absorber	1L EM476	1L EM476
Membrane	5L SWRI-GX	4L SWRI-GX
Retainer	1L EM476	1L EM476
7. Container & Seal Parts Jar, subcover, cover, vent plug	PPO 531-801	PPO 531-801

* 5 ampere rate to 1.25 v/c.

problem, confirming previous tests (2). Hydrogen evolution from Inconel 600 within the core structure of charged negatives is now being investigated. Gassing from the shorted Zn/KOH/Inconel couple is expected but may be controlled by plating the Inconel with silver and amalgamating the silver plate.

Negative plate processing was changed in two areas as the result of problems encountered in the feasibility cell stage. Epoxy cement bonding between the PPO frame and the Inconel core was strengthened by drilling 0.060" diameter holes on 0.5" centers around the core edges and forming epoxy rivets through the Inconel to the PPO surfaces on either side. Bond strength before sterilization was increased from 540 psi tensile shear (bonded surface area) to approximately 2,000 psi sheer strength (epoxy rivet cross-section). Also, pasting of negative active material on the core was delayed until after PPO framing was bonded to each core structure and inspected.

The Model 365 feasibility cell will verify design capability for 3,000 "g" shock for 25 AH size framed plates and the use of silver-plated Inconel 600 core structures.

C. Silver-Boron Composite Structures

A desirable plate core structure should have the physical properties of Inconel and the chemical properties of pure silver. Silver-boron filament composites appear to be capable of these combined properties. A contract has been negotiated with General Technologies Corporation, Reston, Virginia to manufacture composite 2-in. x 4-in. panels. Diffusion bond strength will be evaluated by a peel test and the flexure modulus and strength of a representative sample will be determined. Four sets of manufacturing conditions are to be evaluated. ESB will be given sample panels for heat sterilization tests submerged in 40% KOH. Preliminary tests by ESB show no apparent chemical degradation either from sintering the composite or from attack by KOH solution during 120 hours at 135°C.

II. HEAT STERILIZABLE HIGH IMPACT 5.0 AH CELLS FOR C-SAD

A. Objectives and Past Work

In this task ESB is required to develop a 5.0 AH cell capable of wet sealed heat sterilization for 120 hours at 125°C and after charge a simulated landing impact of 2800 $\pm$ 200 "g" from 113 $\pm$ 2 ft. per second. Engineering and prototype cells have been developed and shocked at 2870 "g" after heat

---

(2) Report for Fourth Quarter 1967, JPL Contract 951296, p. 23.

sterilization. Discharge capacity at 5.0 amps to 1.30 volts varied from 2.3 to 5.0 AH on the formation discharge and during six deep cycles increased slightly. Non-sterile control cells delivered 6-8 AH during the same cycling period. Shock after heat sterilization further reduced discharge capacity to 3.0 AH at 2,400 "g" and 2.5 AH at 3,100 "g".

B. Production Cells

Forty production Model 344 cells were fabricated and shipped to JPL for tests. A change in electrolyte volume and concentration was made to account for the measured loss of water during heat sterilization (0.012 gram/hr. at 135°C) by diffusion through the cell case wall. An additional lot of 80 cells has been completed except for activation and sealing.

C. Activation Methods

Activation methods have been reviewed carefully as a possible source of cell-to-cell variation and low capacity after sterilization. While all cells have been activated under vacuum, the method of introducing the electrolyte has varied, ESB/EMED has normally evacuated each cell pack within its own cell case to 28.5 - 0 +0.5 inch Hg vacuum and injected the proper volume of electrolyte through an adapter. Variation in a.c. impedance and in formation charge capacity was attributed to non-uniform activation and wetting. Erosion of active material from the top edges of negative plates was also observed on cell dissections at the end of cell life and was attributed in part to rapid injection of electrolyte during activation. JPL tests by the ESB resident demonstrated cell-to-cell variation could be reduced by evacuation of a group of cells inverted in a pan of electrolyte in a vacuum chamber. The present activation method consists of:

- Sealing stainless steel activation adapter to each cell.
- Inversion of group of cells into Pyrex tray of electrolyte so that all adapters are well below electrolyte level in tray in vacuum chamber.
- Evacuation for 5 minutes at 28.5 -0 +0.5 in. Hg.
- Slow venting of chamber to ambient pressure which floods cell.
- Stand in upright position for 16 hours.
- Evacuation while inverted to remove excess electrolyte to design residual range.
- Final adjustment at room ambient pressure to a weight design tolerance by addition of electrolyte from syringe.

By this method the average amount of electrolyte received in the flooding stage by 22 Model 344 5 AH cells was 25.3 cc with a range of 24.3 - 26.0 cc and a coefficient of variation of 1.4%. In the vacuum withdrawal stage 4.5 $\pm$ 0.5 cc was removed in the pressure range 24 to 29.5 inch Hg leaving a residual volume of 21.0 $\pm$ 0.3 cc in each cell pack. The difference in volumes of electrolyte in the Model 344 cell before and after withdrawal represents the very small free volume in the cell at seal (4.3 $\pm$ 1.2 cc) which aggravates pressure rise and sealing problems. Close control of activation is essential.

III. HEAT STERILIZABLE-HIGH IMPACT 5.0 AH AND 25 AH BATTERIES

A. Objectives and Past Work

This task requires the design, fabrication and test of cells, a dummy battery, a prototype battery, and manufacture of four 24 volt qualification batteries in each capacity size. Performance objectives are:

- Heat sterilization 120 hours at 135°C.
- Eight month trip to planet and 2800 $\pm$ 200 "g" landing impact from 113 $\pm$ 2 ft. per second.
- Power output of 300 W continuous for design capacity. Energy density of 25 WH/lb. at two capacities:

  130 WH, 5 AH battery and 600 WH, 25 AH battery.

The 5.0 AH cell being developed for the C-SAD spacecraft will become the cell for the 18 cell 5.0 AH battery, and the 25.0 AH cell containing 3/4 framed plates will become the cell for the 18 cell 25.0 AH battery, provided the above requirements can be met. A 23-59% capacity loss has been observed during 120 hours of sterilization at 135°C in the 5.0 AH cell attributed to the absorber-retainer material (EM-476), to volatiles from epoxy sealants, or PPO 531-801 case material, or the SWRI-GX membrane.

B. Model 281 Test Cells

A non-high impact 5.0 AH heat sterilizable sealed cell was designed, using cell jar and sealing components of the high impact 5.0 AH cell, in order to measure the relative effects of suspected materials on capacity loss during sterilization. In the first experiment 21 cells were manufactured to test three epoxy sealants and the principal epoxy sealant at three levels of exposed epoxy surface. One, two, or three areas of the empty cell case were coated with the test epoxy and cured fully per process specification in an oven. Areas of exposure for DEN438-EK85/DMP30 were 1.1, 1.7,

and 2.8 in^2, and for the other test epoxies, Epocast 221/927 and Isochem 811B/811A, the test area was 1.7 in^2.

Table X gives design features of the test cell (Model 281) compared to the C-SAD Model 344 high impact cell. One of the six control cells contained a clear polysulfone window cemented into one narrow cell wall for observing electrolyte level changes during heat sterilization. Table XI summarizes cell weight losses and a.c. impedance changes during 120 hours heat sterilization at 135°C. No significant differences were noted between the three epoxies or between levels of exposed area, or between any epoxy group and the controls.

The cells were then formation charged per process specification: 10-12 ma for 30 hours, then 165 ma to 2.00 volt on first cell in the string (6.01 AH); discharged for 18 minutes at 4.0 amps (1.2 AH out); and finally recharged, at 165 ma to 1.97 volts on each cell. The net capacity gain from the partial discharge and recharge was a mean of 1.14 AH (19%) in each cell. Table XII summarizes formation charge-discharge capacities for each of three cells in the epoxy test groups and the control group. The mean formation input of 7.2 AH (50% theoretical) for the 21 heat sterilized cells is typical of this design, but the hydrogen gas pressures causing 8 of 21 cells to bulge and leak during formation is not. The incidence of leakage appears to increase with increasing area of cured epoxy. Formation input and output capacities of the test groups are not significantly different from control cells. Table XIII summarizes 9 cycles of discharge capacities on the median cells of each test group. Again no significant differences between test groups are seen. During cycling mean capacities increased 29% from a minimum second cycle 4.46 AH to a maximum 8th cycle capacity of 5.78 AH.

It was concluded that the 30-40% capacity loss during 120 hours heat sterilization at 135°C in the 5.0 AH cell design can be attributed to cured epoxy areas only if three epoxy resin-hardener systems from three suppliers all behave almost identically.

C. Reinforced High Impact 5.0 AH Cells

Since previous work had shown the prime failure mode of the Model 344 cell was buckling of plates and struts in the terminals forward shock at 2,800 $\pm$ 200 "g", seven Model 344 cells were constructed with the following design additions:

- Epoxy DEN438-EK85/DMP30 (2.0 cc) in bottom of cell jar to cement positive "U" folds and exposed negative plates to bottom of jar.

- Polysulfone shims cemented to silver sheet plate struts between top of plate and bottom of cell cover.

TABLE XI

EFFECT OF EPOXY SEALANTS ON WEIGHT LOSS AND A.C. IMPEDANCE DURING HEAT STERILIZATION
MODEL 281 TEST CELLS

Epoxy System Resin/Hardener	Area, In^2 Cured Epoxy Exposed	Weight, gms			A.C. Impedance, ohms	
		Before HS	After HS	Loss in HS	Before HS	After HS
DEN438EK85/ DMP30	2.8	166.5	165.0	1.5	1.30	.047
		165.9	164.5	1.4	1.35	.040
n=3		164.0	162.5	1.5	1.30	.047
	1.7	167.0	165.6	1.4	1.34	.047
		166.8	165.6	1.2	1.25	.049
		166.2	164.8	1.4	1.35	.065
	1.1	166.7	165.3	1.4	1.39	.057
		165.6	164.0	1.6	1.30	.042
		165.4	163.9	1.5	1.30	.044
Epocast 221/927	1.7	165.2	163.7	1.5	1.35	.047
		165.5	163.8	1.7	1.28	.040
n=3		165.3	163.8	1.5	1.37	.039
Isochem 811B/811A	1.7	165.1	163.6	1.5	1.26	.041
		164.9	163.5	1.4	1.30	.045
n=3		164.9	163.6	1.3	1.39	.042
Controls	0	164.5 - 165.6	163.1 - 164.0	1.4 - 1.9 $\bar{X}$=1.55	0.95 - 1.44	.041 - .095
n=5						
$\bar{X}$	--			1.48	1.27	.050

Notes: (1) Oven purged with N_2 at rate of 200-300 cc/minute.
(2) Cells supported with metal clamps on broad sides of jar and cover. No darkening of PPO 531-801 jar material observed.
(3) No visible electrolyte leakage nor distortion of case by pressure build-up remaining after HS test.

TABLE XII

EFFECT OF EPOXY SEALANTS ON FORMATION CHARGE/DISCHARGE CAPACITIES
MODEL 281 TEST CELLS

Epoxy System Resin/Hardener	Area, In^2 Cured Epoxy Exposed	Formation Charge Input AH	Discharge Capacity, AH At 3.3A to 1.30V	At 0.7A to 1.30V	Total Output	Mean Input/ Output AH/AH	Efficiency Out/ In %
DEN438EK85/ DMP-30	2.8	7.33L	4.43	0.71	5.14	7.35/ 5.32	72.5
		7.33L	4.54	0.82	5.36		
		7.36	4.56	0.89	5.45		
	1.7	7.65L	4.79	0.84	5.63	7.20/ 5.12	71.0
		7.02L	4.09	0.61	4.70		
		6.93L	3.83	1.20	5.03		
	1.1	7.02	4.37	0.76	5.13	6.96/ 4.92	70.7
		6.89	4.10	0.64	4.74		
		6.93	4.20	0.68	4.88		
Epocast 221/927	1.7	6.80L	4.29	0.67	4.96	6.93/ 4.83	69.8
		6.98	4.10	0.57	4.67		
		7.02	4.24	0.62	4.86		
Isochem 811B/811A	1.7	7.33	4.51	0.72	5.23	7.20/ 5.15	71.5
		7.45	4.79	0.56	5.35		
		6.80L	4.35	0.53	4.88		
Controls, $\bar{X}$	0	7.22	4.39	0.72	5.12	7.28/ 5.14	70.6
n = 6, Range		0.60	0.72	0.86	1.52		
(1 of 6 leaked) $\bar{X}$						7.15/5.08	71.1

NOTES: (1) L = Electrolyte leak near end of formation charge due to excessive hydrogen pressure.
Seven of 8 leaks at case to cover seal. One leak at negative terminal.

TABLE XIII

EFFECT OF EPOXY SEALANT ON DISCHARGE CAPACITY

CYCLE NO.	DEN 438EK85 DMP-30 1.1in^2	DEN 438EK85 DMP-30 2.8in^2	EPOCAST 221/927 1.7in^2	ISOCHEM 811B/811A 1.7in^2	CONTROLS NO EXPOSED AREA
FORMATION	5.03	5.45	4.86	5.23	4.89
1	4.71	4.43	4.56	4.20 (min)	4.44
2	4.68	4.60	4.72	4.85	4.86
3	4.75	4.87	4.73	4.76	4.72
4	4.72	4.55	4.65	4.76	4.86
5	4.86	5.16	4.77	5.16	4.95
6	4.96	5.31	4.68	5.20	4.94
7	5.75	6.31 (max)	5.42	5.86	5.55
8	5.74	6.10	5.44	5.73	5.46
TOTAL:	45.2	46.8	43.8	45.8	44.7

NOTES:

(1) Charge at 0.25 amp (7.5 ma/in^2) to 1.97v all cycles after formation.

(2) Discharge at 3.3 amps (100 ma/in^2) to 1.30v, then 0.7 amp (20 ma/in^2) to 1.30v.

(3) Active Ag per cell = 29.2 gm; efficiency = 0.22 AH/gm max, 0.14 AH/gm min.

(4) All cells heat sterilized sealed for 120 hrs. at 135°C.

(5) Group mean (5 groups) 9 cycle capacity sum = 45.3 on range 3.0 AH. Mean output per cycle = 5.0 AH.

The epoxy plate-lock was intended to hold plates in tension and the polysulfone shims were to stiffen the struts during terminals forward shocks. A serious disadvantage was a reduction in free volume and in electrolyte per cell. Six of the seven modified cells plus two control cells were successfully heat sterilized at 125°C for 125 hours. The PPO 531-801 jar of one cell cracked by air oxidation through a thin section in its silicone protective coating. PPO 531-801 is being replaced by PPO 534-801 which is more immume to oxidation at 125-135°C in air. During the second stage of formation charge the six of six remaining modified cells developed high hydrogen pressure and leaked electrolyte, while the two control cells charged normally. Two modified cells with loss of electrolyte less than 0.3 cc out of 22 cc were equipped with pressure gages and overpotted. During cycling tests the two control cells completed 13 and 15 cycles to short during 3 months of testing. The modified cells shorted after 1 and 2 cycles, respectively.

Post-mortem of the modified cells revealed the platelock epoxy had wicked up the side edges and into the negative plates reducing the negative active material available for charge. Separator corner folds wetted by the epoxy had small holes through all four layers of SWRI-GX membrane which caused the premature shorts. Chemical tests have shown no incompatibility between the epoxy resin, hardener, and SWRI-GX membrane. Physical stresses during heat sterilization may have produced tears at the corners and cell failure.

This epoxy platelock has thus been eliminated as a high impact cell design feature because of the high hydrogen cell pressures (40-50 psig) during post-sterilization formation charge, low input capacities, and subsequent premature shorts during the first two deep cycles.

D. Effect of Absorber and Membrane on Capacity After Sterilization

Kendall EM-476 polypropylene non-woven felt (4 mils dry thickness), used in the Model 344 high impact cell for both positive plate absorber and negative plate retainer, was suspected of contributing to post-sterilization loss. On the other hand, RAI-116, a membrane made by grafting acrylic monomer onto irradiated polyethylene film, considered to be chemically identical to SWRI-GX membrane, was known to give no post-sterilization capacity loss in non-impact 25 AH cells of the Model 345 type sealed with epoxy DEN438-EK85/DMP30. A new novolac epoxy Isochem 811B/811A system appeared to be free of the crazing in large masses experienced in the DEN system. Cell case material PPO 534-801 was found less sensitive to oxygen attack during heat sterilization in air. To test these design features eight Model 281 test cells were manufactured, sealed, wet heat sterilized 120 hours at 135°C successfully without leakage and then given a formation charge and discharge. Data through this first cycle is

summarized in Table XIV. The percentage improvements in performance observed to date for the major design changes are:

Formation Charge Capacity, AH	Range AH		$\bar{X}$	Gain %
	Min.	Max.		
- Control - 6 cells, EM-476 retainers and absorbers, 5L SWRI-GX membrane	6.89	7.55	7.22	0
- No EM-476, 6L SWRI-GX membrane n = 4	7.43	9.19	8.02	+11
- No EM-476, 6L RAI-116 membrane n = 4	9.99	10.15	10.05	+39
Formation Discharge Capacity, AH				
- Control, n = 6, same as above	4.74	5.62	5.11	0
- No EM-476, SWRI-GX, 6L	5.33	6.95	5.91	+16
- No EM-476, RAI-116, 6L	7.83	7.94	7.90	+55

Respectable performance has thus been achieved for the first time in this size cell by omission of EM-476 polypropylene absorber-retainer material and the substitution of RAI-116 for SWRI-GX membrane as the cell separator system. Performance in cycling to failure will be followed closely to determine whether this major performance increase is maintained. Epoxy sealant and case material effects do not appear significant at this point in the experiment.

IV. TASK X HEAT STERILIZABLE 200 "g" IMPACT HIGH CYCLE LIFE BATTERY

A. Objectives and Past Work

This 30 month development program requires design, test, and manufacture of four 18-cell 1200 watt-hour batteries per JPL Specification GMP50436-DSN-B and capable of 400 50% depth cycles after heat sterilization wet-sealed, interplanetary travel, and a soft landing on Mars. Twenty-five AH test cells have been designed, manufactured, heat sterilized 120 hours at 125° C, and then cycled at discharge rates from 5 amps to 38 amps. No

TABLE XIV

EFFECT OF MEMBRANE, EPOXY SEALANT, AND CELL CASE MATERIAL ON FORMATION CYCLE CHARGE-DISCHARGE PERFORMANCE
MODEL 281 TEST CELLS

Separator and Retainer Material	RAI-116				SWRI-GX			
Epoxy Sealant	DEN-438 EK85/DMP30		Isochem 811B/811A		DEN-438 EK85/DMP30		Isochem 811B/811A	
Type of PPO Container	531-801	534-801	531-801	534-801	531-801	534-801	531-801	534-801
Cell No.	I	II	III	IV	V	VI	VII	VIII
Volume of Electrolyte (cc)	23.1	23.2	23.0	23.1	24.4	24.2	24.2	24.6
Weight before Heat Sterilization (gms)	161.2	161.8	160.3	161.8	162.1	162.3	163.3	163.0
Weight Loss during Sterilization (gms)	1.2	1.1	1.2	1.3	1.3	1.1	1.2	1.1
A.C. Impedance before Heat Sterilization (ohms)	0.75	0.77	0.69	0.71	0.54	0.58	0.84	0.72
A.C. Impedance after Heat Sterilization (ohms)	0.12	0.13	0.13	0.10	0.09	0.09	0.11	0.11
Theoretical Capacity of Compound 323-43, AH	0.51	0.51	0.51	0.51	0.51	0.51	0.51	0.51
Amp. Hrs. to 1.60 V	0.47	0.44	0.42	0.47	0.46	0.43	0.45	0.45
Formation Charge Input, Step 1 (AH)	9.29	9.05	8.60	8.45	5.84	5.33	5.19	5.33
Net Gain after Partial Discharge (AH)	0.73	0.94	1.44	1.70	3.35	2.24	2.24	2.56
Total Input (AH)	10.02	9.99	10.04	10.15	9.19	7.57	7.43	7.89
Total Amp-Hrs/gm Ag	0.36	0.36	0.36	0.36	0.32	0.27	0.26	0.28
Formation Discharge:								
@3.3 amps to 1.30V (AH)	6.21	6.18	6.19	6.52	5.59	4.47	4.12	4.43
@0.7 amps to 1.30V (AH)	1.73	1.74	1.64	1.40	1.36	1.35	1.21	1.13
Total (AH)	7.94	7.92	7.83	7.92	6.95	5.82	5.33	5.56
Total AH/gm Ag	.282	.281	.277	.281	.246	.206	.189	.197
% of Chg. Acceptance	79	79	78	78	76	77	72	71

NOTES:
- o - Electrolyte: 40% KOH with 91.0 gm ZnO/l.
- o - Cells heat sterilized 120 hours at 135°C after sealing.
- o - Formation constant current charge profile:
  - (1) 0.016 amp to last cell in string reached 1.60 V.
  - (2) 0.170 amp to 2.00 V on individual cells (step 1).
  - (3) Partial discharge at 0.10 amp for 15 hours.
  - (4) 0.170 amp constant current to 2.00 V on individual cells (step 2).

leakage has been observed to date. Capacity maintenance through seven 100% depth cycles is above 25 AH at rates to the 1C rate for both heat sterilized and control cells.

B. Evaluation of Pellon 2530W Absorber Material

Screening tests were conducted on Pellon 2530W polypropylene-latex absorber material before and after dry and wet heat sterilization. Table XV is a summary of the test data. Pellon 2530W is the production designation of Pellon 14019 selected by Texax Instruments (3) for wet heat sterilizable Ni-Cd sealed cells and is the present mostly likely substitute for Kendall EM-476 polypropylene. Neither material is dry heat sterilizable. Pellon 2530W exposed 16 hours at 135°C increased in dry thickness 83% and became very friable. Sterilization in 40% KOH at 135°C for 120 hours increased wet thickness 58%, electrolyte retention 45%, and decreased the roll direction length by 10%. Increasing electrolyte concentration from 30% to 40% KOH increased room ambient wetting time of non-sterile samples from 32 seconds to 10-20 minutes when submerged.

Pellon 2530W will be tested as the positive plate absorber in 25 AH cells.

C. Cycling Tests

A preliminary 15 cell cycling test program was considered necessary to prove out cycling circuits and the reliability of the experimental cell seal design for survival of the heat sterilization of 120 hours at 135°C. Table XVI gives the experimental design. The effect of negative additive at levels of 3, 5, and 7 percent and the effect of Pellon 2530W positive plate absorbers will be measured. Cell pack design is quite similar to the Model 345 cell described previously. (4)

V. TASK XI HEAT STERILIZABLE 200 "g" IMPACT 2000 WATT-HOUR BATTERY

A. Objectives and Past Work

In this 12 month program ESB has designed the Model 364 18-cell 24 volt 80 AH sealed ZnO/KOH/Ag battery to be capable of 120 hours wet sealed heat sterilization at 135°C, formation charge, flight acceptance testing, interplanetary travel, a soft landing, followed by at least 4-100% depth cycles of charge-discharge. Cell design is complete. Battery design is complete to dummy battery stage. Projected performance at the C/4 discharge rate is 43 WH/lb of cell after heat sterilization.

---

(3) JPL Contract 951972, First Quarterly Progress Report, p. 12.
(4) Report for First Quarter, JPL Contract 951296, p. 50.

TABLE XV

PELLON 2530W ABSORBER MATERIAL CHARACTERISTICS

Test Parameter	Unit	Mean Value, n = 5		
		Before Heat Sterilization		After Heat Sterilization (1)
1. Electrolyte	% KOH	30	40	40
2. Weight	mg/in^2			
Dry		34	35	38
Wet, 1 hr.		137	162	
Wet, 200 hrs.		154	180	285 (1)
3. Wet Out Time	Sec.	32	(2)	
4. Wicking				
Height (4)	in.	0.25	0	
Time	hr.	72	120	
5. Thickness	mil.			
Dry		10.1	10.6	19.4 (3)
Wet, 1 hr.		10.2	10.8	
Wet, 200 hrs.		10.9	11.6	17.8 (1)
6. Electrolyte Retention	%			
Wet, 1 hr.		402	464	
Wet, 200 hr.		450	510	740 (1)
7. Density	$mg/in^2/mil$			
Dry		3.4	3.2	2.0 (1)
Wet, 1 hr.		13.4	15.0	
Wet, 200 hr.		14.0	15.4	16.2 (1)
8. Dimensional Change	%			
Length, roll		-1	-1	-10
Width		0	0	0

NOTES: (1) 120 hrs. at 135°C
(2) Did not wet in 72 hour test on surface of KOH. Submerged samples wet in 10-20 minutes.
(3) After washing and drying.
(4) Vertical suspension test. All samples wicked 1 inch in 9 minutes when sample surface rests on adjacent wall of cell jar.

TABLE XVI

PRELIMINARY CYCLING TEST DESIGN

A. Design Variable	Test Cell Set and Serial Number														
	1 (NS)			1 (S)			2			3			4		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1. Control - Non-Sterile	X	X	X												
2. Control - Sterile				X	X	X									
3. Negative Additive (Compound 323-43)															
3%													X	X	X
5%										X	X	X			
7%	X	X	X	X	X	X	X	X	X						
4. Positive Plate Absorber (1L Pellon 2530W)							X	X	X						
5. No Absorber 5L-SWRI-GX Membrane 1L-SWRI-GX retainer	X	X	X	X	X	X				X	X	X	X	X	X

B. Common Design Features

1. Active Material:
   Positive - 96.6 g Ag, 69.4 g/in^3
   Negative - 66.5 g ZnO, 49 g/in^3

2. Plate Grid
   Positive - 1/0 Ag
   Negative - 2/0 Ag

3. Electrolyte - ESB SS-234 (M40)

4. Negative Active Material Binder - 2% Teflon 7, unsintered.

5. Plate area - 96 in^2 (positives)

B. Fabrication of Cells

Cell jars JPL P/N 1-074 were molded successfully by plastic Mold and Engineering, East Providence, Rhode Island using GE PPO 534-801. Cell covers have been machined from sheet stock of the same material. Seals between cover and jar and terminals to cover will be epoxy. An experiment is in progress to determine which of two epoxies and a control (Epocast 221/927 used successfully on the Model 345-25 AH cell or Isochem 811B/A) is the most reliable seal. Dummy cells without plates were fabricated, activated to a level equivalent to plate height, sealed, sterilized 120 hours at 135°C, then temperature-vacuum cycled and pressurized to destruction. The cell with the control epoxy DEN438-EK85/DMP30 developed visible cracks in the cover to jar seal fillet as expected. Isochem 811B/A was unaffected by the same treatment. Weight loss of electrolyte (as H_2O) was 0.2% in both cases without observable KOH leakage. Temperature cycling (after heat sterilization) between the extremes of -10°C to +55°C had no apparent effect on the seals. A subsequent vacuum test on the sealed cells at 25 in. Hg for 13 hours without cell supporting clamps showed no leakage. Two cells were pressurized unsupported with water and failed in the range 80 to 90 psig considered adequate for the prototype machined cover design. The mode of jar failure in both cells was bulging of the 3.7" W x 4.3" H broad walls, and cracking along the cover seal flange and then down the narrow wall. In this test Isochem 811B/811A and Epocast 221/927 performed equally well for the terminal to cover seal.

Nine cells have been manufactured for evaluating electrochemical and environmental performance characteristics. No major production problem has been encountered. Two of three non-sterile cells and one sterile cell have clear polysulfone windows in the jar wall to permit visual observation of electrolyte level and plate edge conditions. Sterilization tests begin April 8, 1968.

Silver plate tabs in present designs are not insulated between the cover seal and the top plate edge. Three Teflon coatings were applied to samples by Livingstone Coating Corporation, Charlotte, N. C. for evaluation through heat sterilization in 40% KOH. Sample coating types and results are below:

- 5 coats Teflon FEP, green - coating peeled off part of sample with 1.4% weight loss.
- 3 coats Teflon FEP, green - same as above.
- 2 coats Teflon FS, black - coating peeled completely off sample during 120 hours at 135°C.

C. Battery Development

Prototype ESB Drawing 364-1000 and referenced drawings are 60% complete. A dummy 18-cell battery is being manufactured to evaluate interactions of all materials in the Model 364 battery between chassis and cells during heat sterilization and thermal cycling. The aluminum honeycomb chassis has been designed and ordered with delivery scheduled for May 1968. Materials have been selected to minimize weight, to be heat sterilizable at 135°C, to be matched in linear expansion coefficients, and to provide adequate strength to support cell walls. Table XVII lists materials under c onsideration at this time.

VI. QUALITY ASSURANCE

Positive plate, negative plate, and cell assembly quality control travelers were generated for the Model 344 production cells and delivered with each cell shipped to JPL. Inspection flow diagrams of parts, materials, and processes for Model 344 cells have not been released pending anticipated design changes to reinforce the positive and negative plates for the 3,000 "g" shock.

Cells received all inspections per applicable Inspection Operation Sheets. Sixteen of 52 Model 344 cells manufactured during this period were rejected and reworked to print when subcovers were found cemented at an angle. In 20 of 52 cells alignment of holes drilled in plate struts was not adequate to accept the shock absorbing rod insert. These plates were reworked and reassembled with new SWRI-GX membranes. A drawing change was made to elongate the hole in the $\pm$ X direction to reduce assembly problems without sacrifice of plate alignment in the more critical $\pm$ Y direction.

CONCLUSIONS AND FUTURE WORK

1. Longer sterilization periods in the sealed condition cause greater capacity losses in silver-zinc oxide cells than do shorter sterilization periods.

2. Efforts to demonstrate that one or more of the organic constituents cause capacity losses during sterilization have given ambiguous results. The apparatus has been redesigned.

3. In silver-cadmium cells ultimate failure of sterilized systems was due to silver penetration of SWRI-GX. Longest life was found in floated cells as compared to cycled cells or cells left on charged stand.

4. The 3/4 framed Inconel supported 25 AH feasibility cell has been modified in negative plate assembly to increase shock strength

TABLE XVII

PHYSICAL PROPERTIES OF 2000 WHR BATTERY CHASSIS, POTTING, AND CELL CASE MATERIALS

Material and Application	Coefficient Linear Expansion ($X10^{-6}$ in/in°F)	Density (lb/in^3)	Tensile Strength ASTM Method D638 ($10X^3$ psi)	
			75°F	200°F
1. Battery Container				
• Magnesium A231B-0	14.8	0.064	37	29
• Titanium Ti75A	5.1	0.164	80	64
• Aluminum 5052-0	13.2	0.097	28	27
• Aluminum 6061-T6	14.1	0.098	38	35
2. Potting				
• Stycast 1090	10.6	0.028	--	--
• Solithane 113-1	60	0.039	0.40	0.46
• Silicone RTV11	130	0.042	0.35	--
3. Cell Cases				
• GE-PPO 534-801	29	0.038	11.6	8
• GE-PPO 531-801	29	0.038	10.5	6
4. Cell Terminals				
• Copper, annealed	9.8	0.323	32	--
• Silver, annealed	10.9	0.379	27	--
• Inconel, 600 hard	9	0.304	120	--

and improve productibility. Inconel strengthened positive plates reached a maximum pressure of 30.5 psig during 120 hour heat sterilization at 135° C and showed no positive pressure after cooling to room ambient.

5. Vacuum activation procedures for 5-AH sealed heat sterilizable cells have been improved in control of electrolyte quantity per cell and the introduction of electrolyte without plate washing.

6. Tests on fully cured epoxy areas within the 5 AH sealed cell show that three epoxy resin-hardener systems all give only 50% theoretical charged input (7.2 AH) and excessive hydrogen pressures causing leakage in 8 of 21 cells. Six of six cells using the control epoxy DEN438-EK85/DMP30, introduced around the plate pack as a plate-lock and cured in contact with the cell pack, passed sterilization tests but leaked electrolyte during formation charge. The epoxy plate-lock concept to improve shock capability has been discarded.

7. Elimination of polypropylene absorbers and retainers from 5 AH cells has increased formation charge input 11%, discharge output 16%. Replacement of SWRI-GX membranes with RAI-116 has increased formation charge input 28% and output 39%. The effects of cell case material (PPO 534-801 vs. PPO 531-801) and epoxy sealant (minimum surface exposure) were not significant.

8. Teflon FEP (green) and S (black) coatings on silver sheet peel off during 120 hours at 135° C in 40% KOH and are not suitable as tab insulators.

9. Development of 200 "g" shock soft landing 2000 WHr battery is on schedule. Eighty ampere-hour cells and an 18-cell dummy battery are scheduled for sterilization and cycling tests in the next quarter.